Chapter 3 : Alkenes and Alkynes.

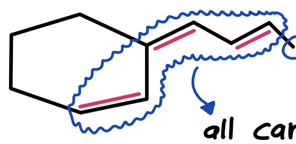
* **Introduction** : They are unsaturated hydrocarbons, alkenes have C=C and general formula C_nH_{2n} (as Cycloalkane). Alkynes have C≡C and general formula C_nH_{2n-2} (as Cycloalkenes).

* Note : whenever we add π-bond, we remove (2H).
  - C−C ⟶ C_nH_{2n+2}
  - C=C ⟶ C_nH_{2n}
  - C≡C ⟶ C_nH_{2n-2}

* Examples :-  ⟷ (isomers) $CH_3-CH=CH-CH_3$ C_4H_8

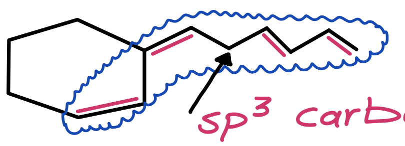
  $CH_3-C≡C-CH_3$ C_4H_6

* Cumulated structure :- C=C=C (middle C → sp)
* Conjugated structure :- C=C−C=C−C=C−C=C (C → sp^2; the circled double bond → It can be Triple bond.)



⟶ [Conjugated].

* Isolated structure :- C=C−C=C−C−C=C−C=C−C=C
  - (C=C−C=C : Conjucated; C=C−C=C−C=C : Conjugated; middle C : sp^3 carbon)



⟶ [Isolated].

* Nomenclature of alkanes and alkynes :-
  * Use the Same IUPAC rules that mentioned for alkanes except :-

a) Select the longest carbon chain that contains Both C=C / C≡C

b) Number the chain from the end nearer to double or triple bond.

* [If numbering is equidistant] ⟹ number the chain from end nearer to 1st substituent

⇓ If equidistant

⟸ number the chain from end based on alphabatical order of substituent

c) Indicate the position of C=C or C≡C, using a lower number.

d) The parent name is ended by:

~~~~ ene for alkene   ~~~~ yne for alkyne

* Examples of alkenes:

$H_2C=CH_2$
Ethene
(Ethylene) → common name

$CH_3-CH=CH_2$
propene

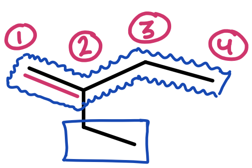
① $H_2C=$ ② $\underset{H}{C}-$ ③ $\underset{H}{C}-$ ④ CH_3
1-butene

$H_3C-CH=CH-CH_3$
2-butene

④ CH_3- ③ $\underset{H}{C}=$ ② $\underset{CH_3}{C}-$ ① CH_3

→ From left the double bond located as (2) similar to from right ⇓ equidistant ⟹ nearer sub

2-Methyl-2-butene



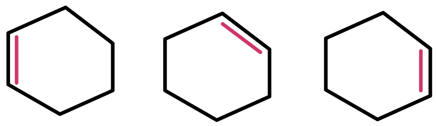
→ 2-Ethyl-1-butene

① CH_3- ② $\underset{Br}{C}=$ ③ $\underset{Cl}{C}-$ ④ CH_3

2-Bromo-3-chloro-2-butene ← [Alphabetical order]

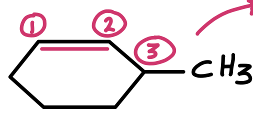
Cl ③ CH_2- ② $\underset{H}{C}=$ ① CH_2 → 3-chloropropene
~~~~

* For Cycloalkenes :-



Cyclohexene

(C_nH_{2n-2})



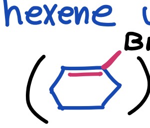
→ 3-methyl Cyclohexene

→ If the Cycloalkene has a substituent :

- → Give number 1 for Carbon of C=C (2) (1)
- → The second carbon should have 2.
- → Give substituent the least number.

→ why we didn't put (1) before Cyclohexene ? because we always start naming from the alkene.

except → we should put 1 before Cyclohexene when the sub. is on the first C-double bond



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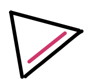
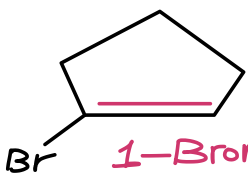
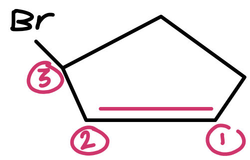


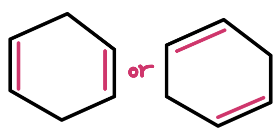
Cyclopropene



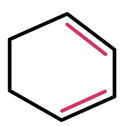
1—BromoCyclopentene



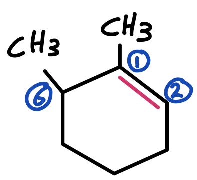
3—BromoCyclopentene



1,4-Cyclohexodiene



1,3-Cyclohexadiene



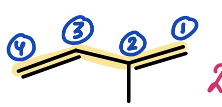
1,6—Dimethyl CyClohexene not (2,3-Di —).

(4) (3) (2) (1) ← (The same)

$H_2C=CH-CH=CH_2$

(1) (2) (3) (4)

→ 1,3- butadiene not (1,3-dibutene)



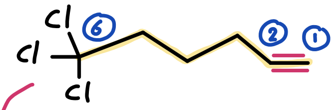
2-methyl—1,3- butadiene

$H_2C=CH-CH=CH-\underset{H}{C}=H_2$

→ 1,3,5— hexatriene

* Examples of Alkynes :-

$H-C\equiv C-H$ → Ethyne (Acetylene) — Common name



→ 6,6,6 – Trichloro – 1 – hexyne

$CH_3-C\equiv C-CH_3$ — 2-butyne (if → 1-butyne)

* Notes :-

1 If molecule contains $C=C$ and $C\equiv C$:-

a) $C=C-C-C\equiv C-C$ } → From right : 2,5 ; From left : 1,4 } start numbering : alkene
→ choose the lower

b) $C-C=C-C-C-C\equiv C$ } → From right : 2,5 ; From left : 1,4 } start numbering : alkyne

c) $C=C-C\equiv C$ } Equidistent ???
start numbering from alkene.

* $\overset{(1)}{H_2C}=\overset{(2)}{CH}-\overset{(3)}{C}\equiv\overset{(4)}{CH}$

1-butene-3-yne (1-butene: first ; 3-yne: parent)

$\overset{(1)}{H_2C}=\overset{(2)}{CH}-\overset{(3)}{C}\equiv\overset{(4)}{C}-Cl$

4-chloro-1-butene-3-yne

$\overset{(5)}{H_3C}-\overset{(4)}{CH}=\overset{(3)}{CH}-\overset{(2)}{C}\equiv\overset{(1)}{CH}$ 3-Penten-1-yne

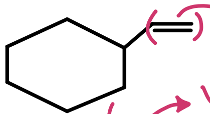
* note :- when $C=C$ and $C\equiv C$ are presented in the Same molecule we always start the name with alkene then alkyne regard the numbering.

2 $CH_2=CH$ is called Vinyl (common name)

$H_2C=CHCl$ → Vinyl Chloride (chloro-ethene)

3 $H_2C=CH-CH_2$ is called Allyl

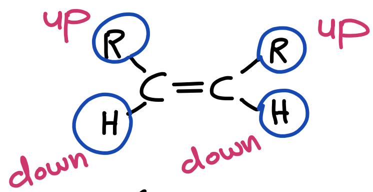
$H_2C=CH-CH_2Br$ Allyl Bromide (3-Bromo propene)



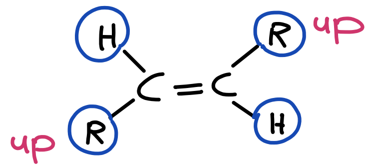
$CH=CH_2$ → vinyl

Vinyl Cyclohexane

* Cis – Trans isomerism in Alkenes :-



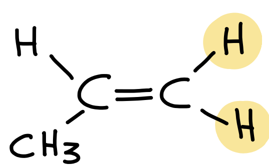
(Cis)



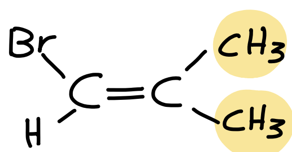
(trans)

* Cis and Trans are part of IUPAC name and should be written in the beginning.

* note : If alkene has identical groups (atoms) on the same carbon of C=C, there is no Cis nor trans.

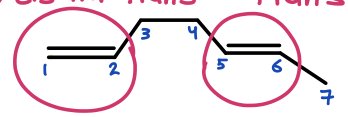


identical

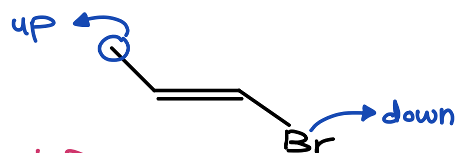


identical

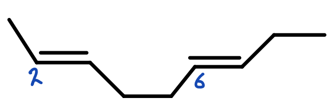
no cis nor trans   trans



trans-1,5-hebtadiene

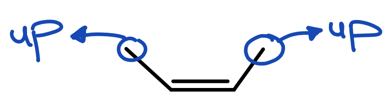


trans-1-Bromopropene



(2-trans, 6-trans) – 2,6-nonadiene.

↳ you can write it without 2 and 6 since the first to first and second to second.



cis-2-butene

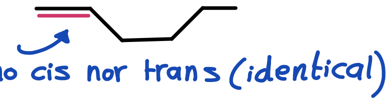
↳ not identical because CH_3/CH_3 is not on the same carbon.

* Ex : Which one can show Cis-trans isomerism ?

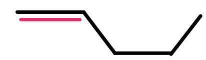
1-hexene , 1-pentene , 2-methyl-2-pentene , 2-hexene , 3-hexene

2-methyl-2-butene.

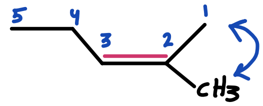
1. 1-hexene →



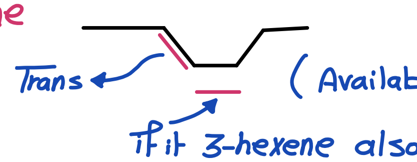
2. 1-Pentene



3. 2-methyl-2-Pentene



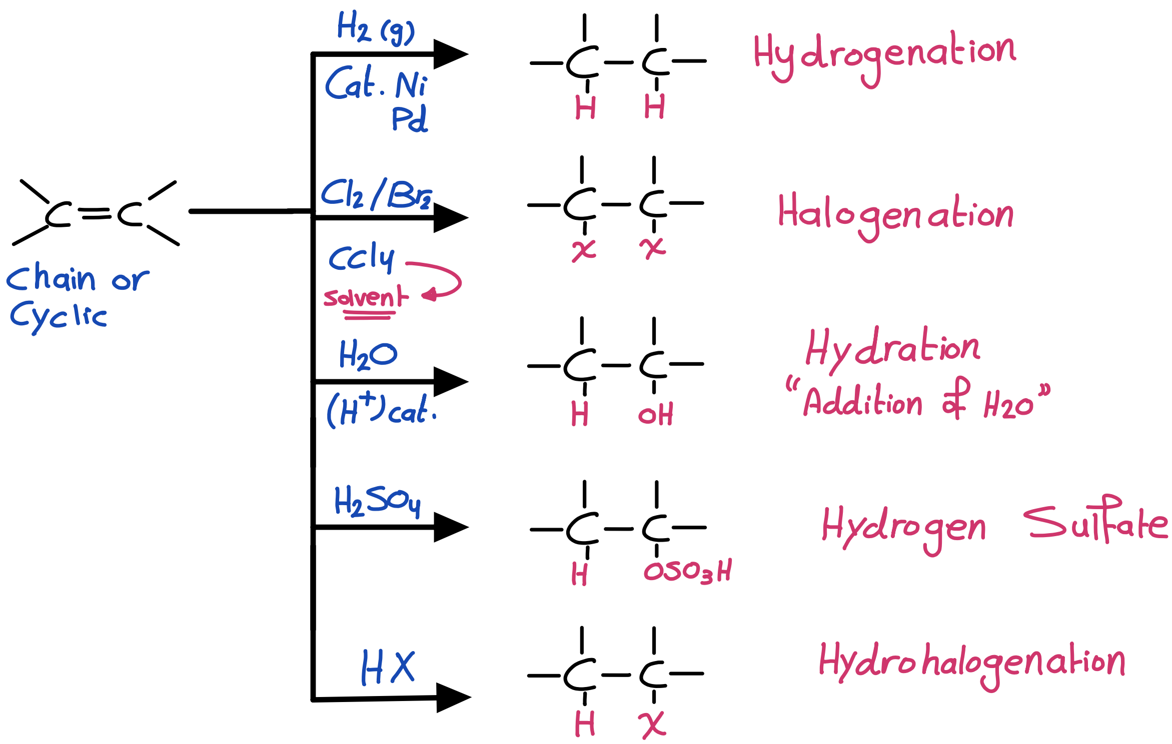
4. 2-hexene

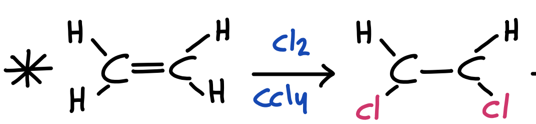


* Reactions of AlKenes and AlKynes :

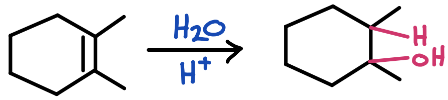
First For AlKenes :

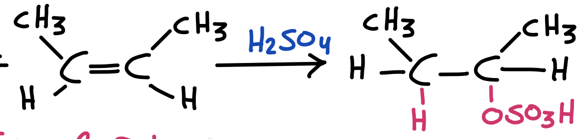
π bond is broken in reactants and new σ bonds are formed in the product ⟹ This type of reaction is called Addition reaction .





→ $CH_2Cl\,CH_2Cl$ (1,2-dichloroethane)

* 

* 

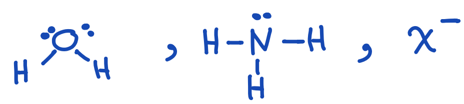
Cis-2-Putene

* Mechanism of reaction :-

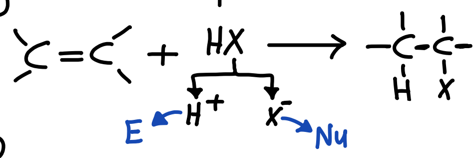
* Electrophile (E) : electron-deficient (ether +/±) species, such as : H^+, $\overset{+}{C}H_3$, $AlCl_3$

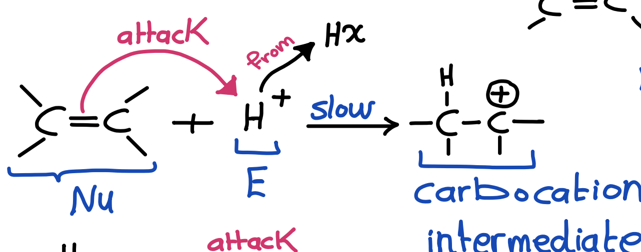
* Nucleophile (Nu) : electron-rich species (−/±). such as : π-bond in alkene or benzene

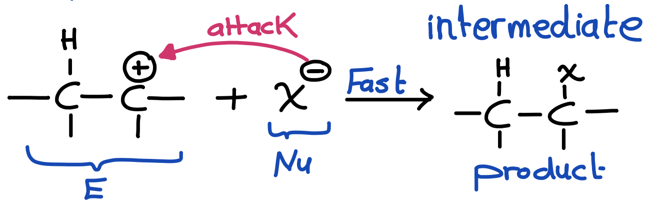
→ contains (ē) which is negative.



Now, Mechanism of reaction is consisting of 2 steps.

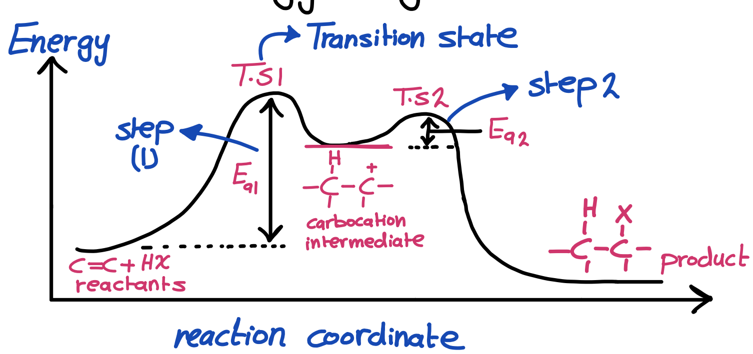


* step 1 :- 

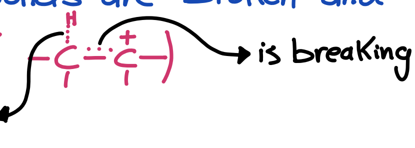
* step 2 :- 

* mechanism :- [Electrophilic Addition reaction] for alkenes and alkynes

* Reaction energy diagram :



* T.S : Transition state : Bonds are broken and formed at same time.
↳ before intermediate (



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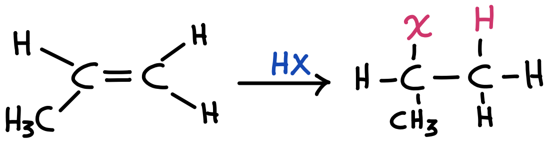
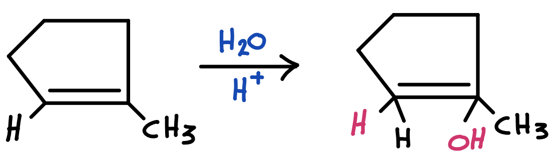
* Ea : Activation energy (↳ endothermic) : Difference in energy between reactant and Transition state or intermediate and Transition state.

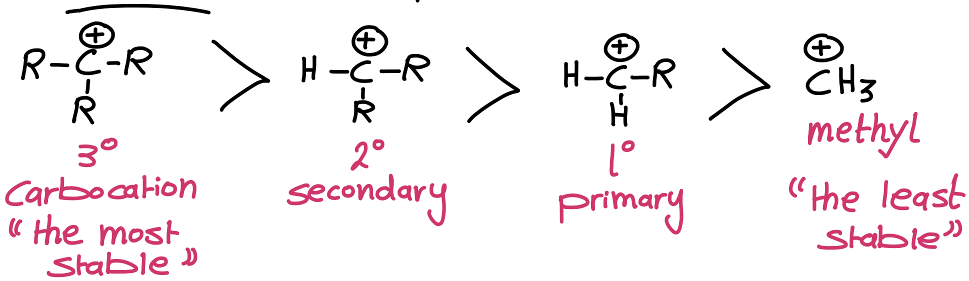
* Reaction is exothermic ($\Delta H_{rxn} < zero$).
* Ex.1 : Write an intermediate for the following reaction.

* Markovnikov's rule : It is important if alkene (or alkyne) is not symmetrical.

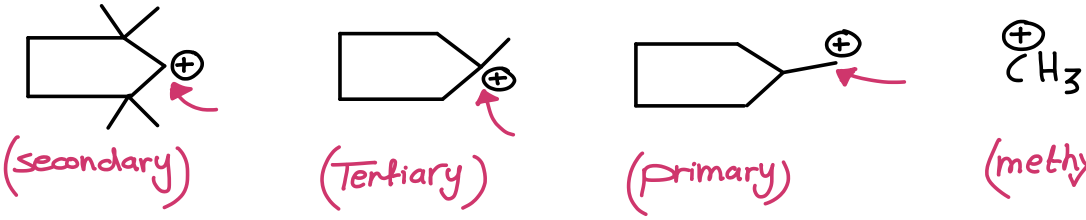




* Markovnikov's rule states that :
Electrophile (H^+) is added to Carbon of C=C that has more hydrogens that are attatched directly to the carbon.
* Explain : stability of Carbocation

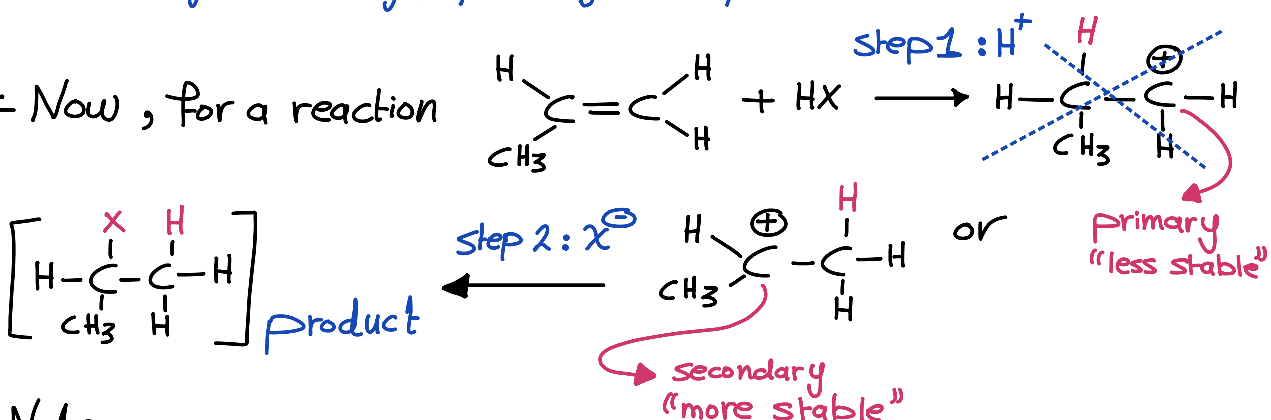


* Ex.1) Arrange the stability of Carbocations :



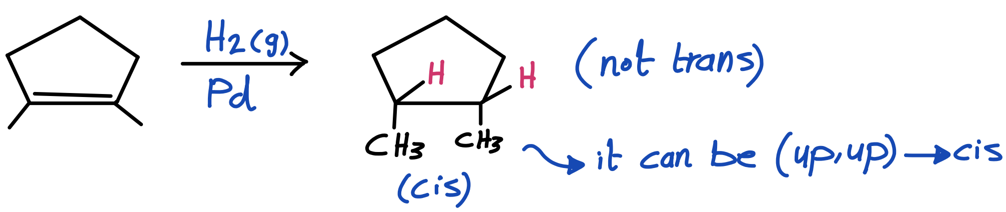
Tertiary > Secondary > primary > methyl

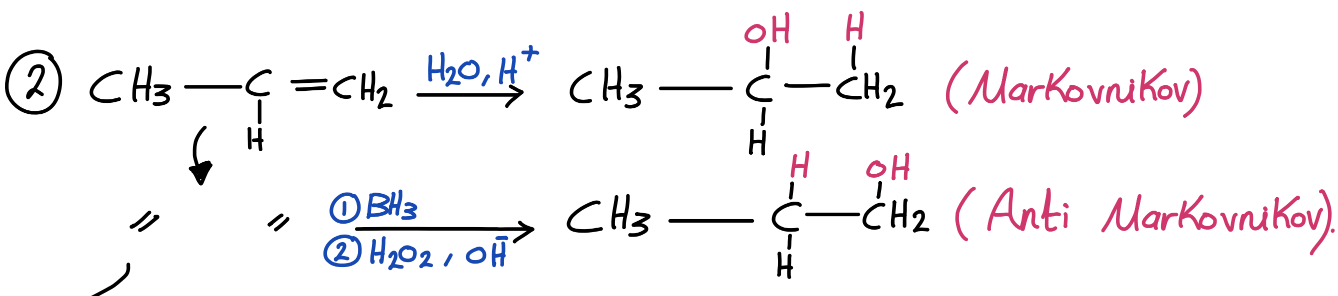
* Now, for a reaction



* Notes :

① For Cyclic alkene with substituents.

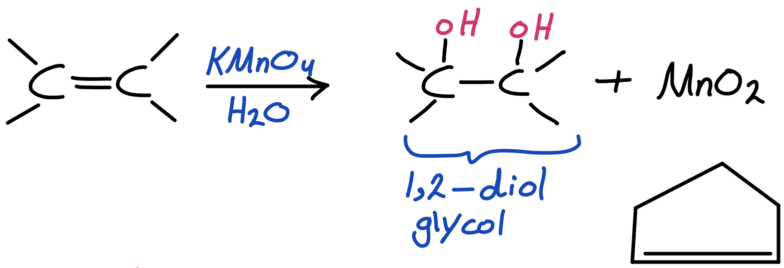


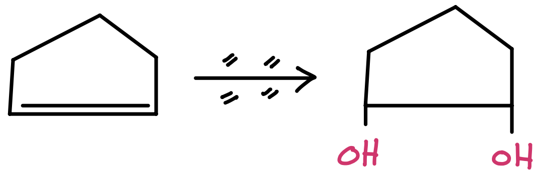


Last rxn is called : (Hydroboration oxidation) of alkenes.

✳ Finally, for reactions of alkenes ⇒ there is an Oxidation Reaction.

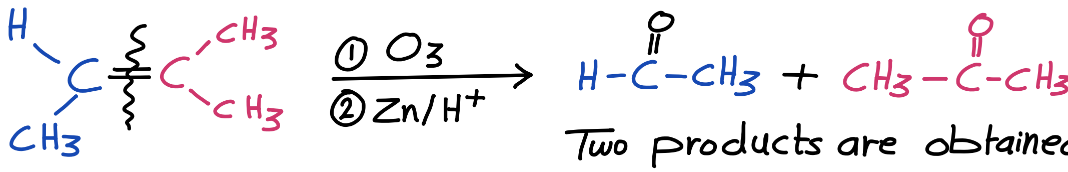
① Oxidation using $KMnO_4$ → oxidizing agent (→ number of oxygen atom increased.)



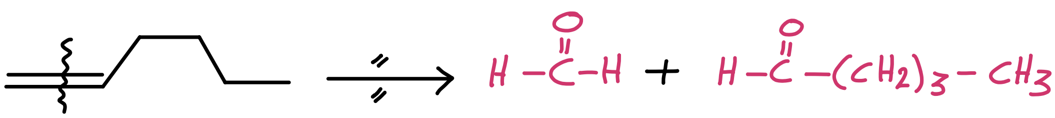


(O_3 < $KMnO_4$) oxidizing agent

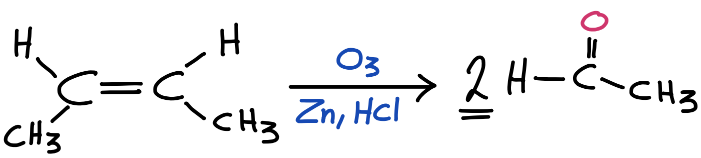
② Ozonolysis using O_3 then Zn/H^+.

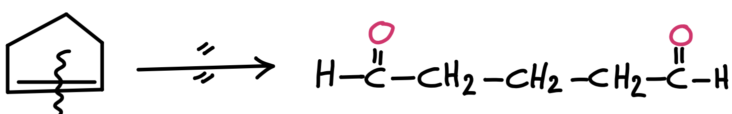
a) 

Two products are obtained.

b) 

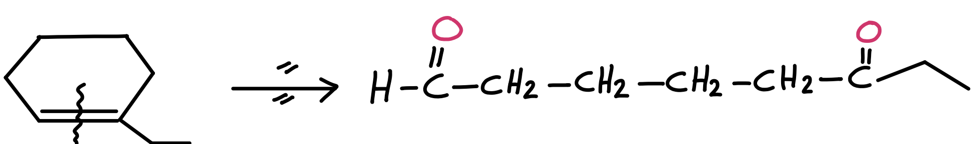
✳ σ and π bonds are broken of C=C.





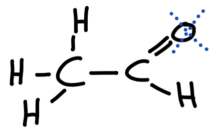
break at σ and π bonds

1 product is obtained

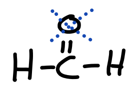


Only 1 product is consumed

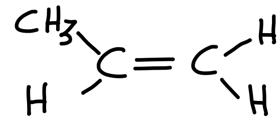
* EX : Draw an alkene that upon ozonolysis will produce



and



. Answer



* Draw an alkene that upon ozonolysis will produce only

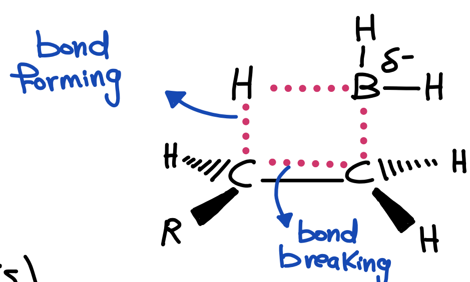
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$.

* General Examples :-

① $CH_3-CH=CH_2 \xrightarrow[\text{② } H_2O_2,\ OH^-]{\text{① } BH_3} CH_3-\underset{H}{CH}-CH_2OH$ (Anti Markvnikov)

② $CH_3-CH=\overset{*}{C}H_2 \xrightarrow{BH_3} H_3CCH_2CH_2C-B(\overset{*}{C}H_2CH_2CH_3)_2$ ("3")

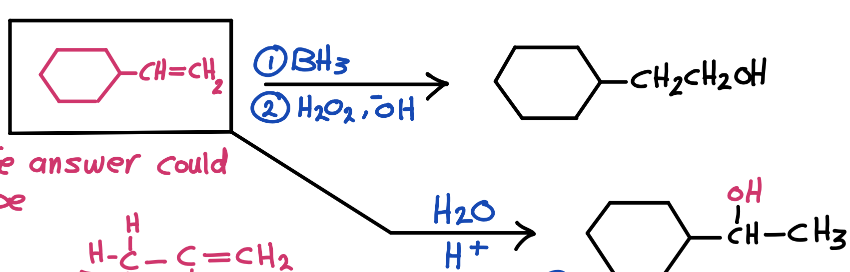
③ Draw the transition state for the above reaction



(This reaction is related to 1+2)

④ $(CH_3CH_2\overset{*}{C}H_2)_3B + H_2O_2 + {}^-OH \longrightarrow 3\,CH_3CH_2CH_2OH$

⑤

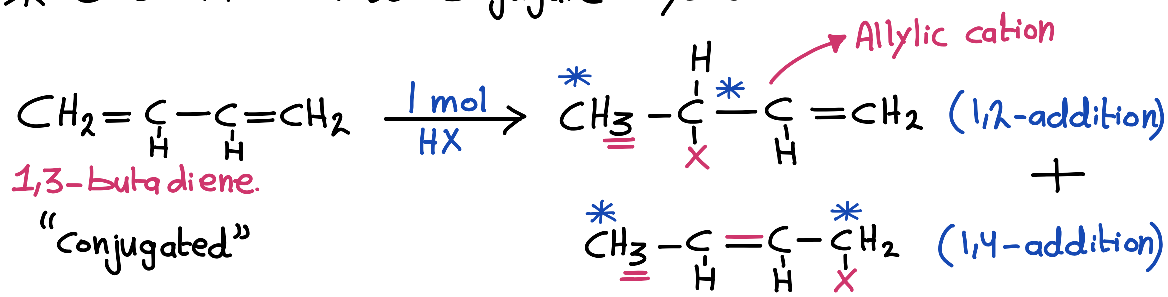


The answer could be

$H-\underset{H}{\overset{H}{C}}-\underset{CH_3}{C}=CH_2$

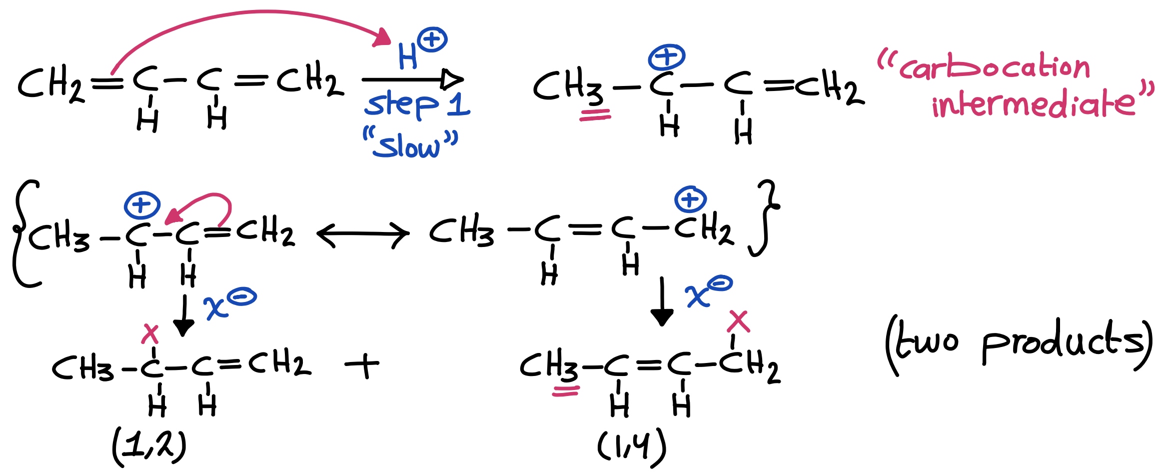
⑥ Methyl propene $\xrightarrow[Pd]{H_2(g)} H-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3$

* 3.15 : Addition to Conjugate Systems.

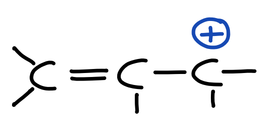


* Two products are obtained, 1,2-addition and 1,4-addition products. MarKovniKovs rule is applied.

* Explain. 1,4- addition product

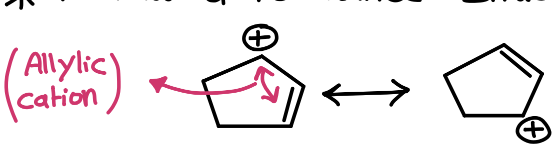


* Allylic Cation



Remember : methyl, 1°, 2° and 3° carbocations.

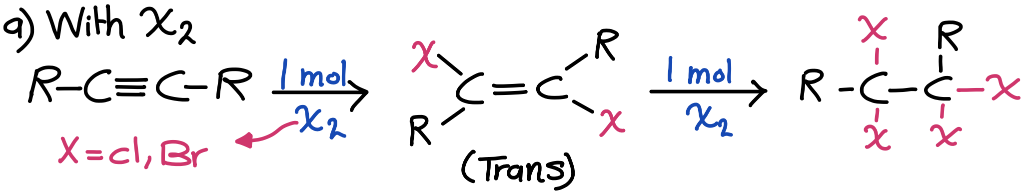
* Draw a resonance structure for the following allylic carbocation.

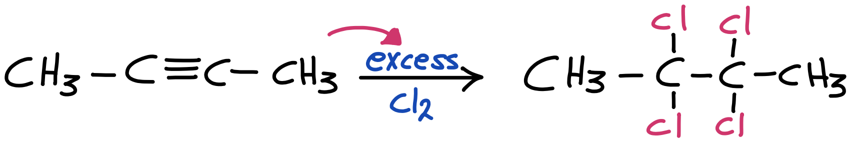


Note : Allylic carbocation is stable due to the [delocalization] of the positive charge.

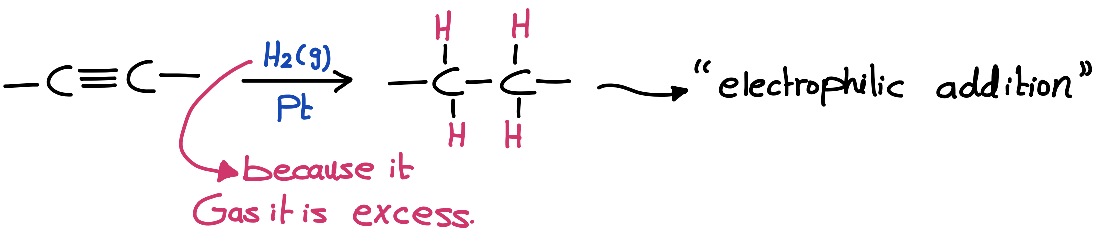
* Reactions of Alkynes :

a) With X_2

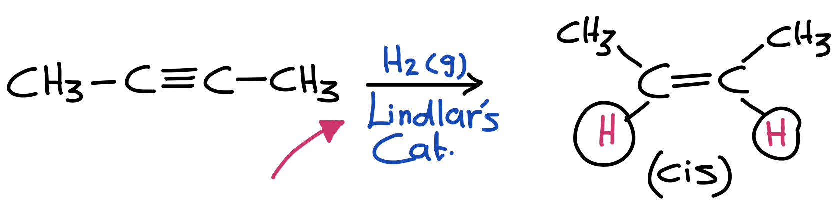


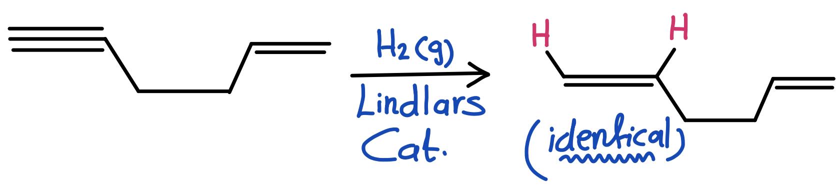


b) With H_2 (g) , Cat. Pt or Ni

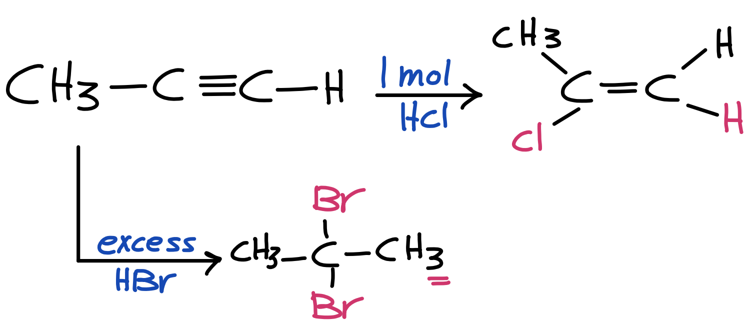


But in the presence of Lindlar's catalyst : alkene isn't affected and just 1π bond is broken in alkyne and cis – product is obtained.



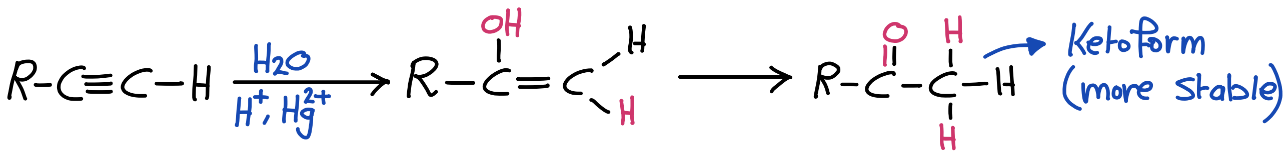


c) With HX : Markovnikov's rule is applied for R–C≡C–H.

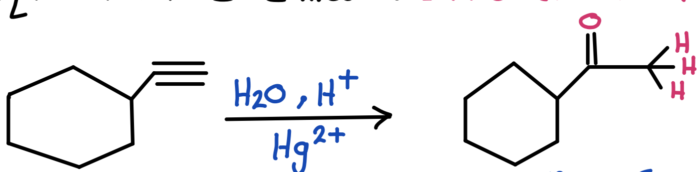


d) With H_2O, H^+ and $HgSO_4$ (Hg^{2+}).

1 π bond is only broken and Markovnikov's rule is applied.



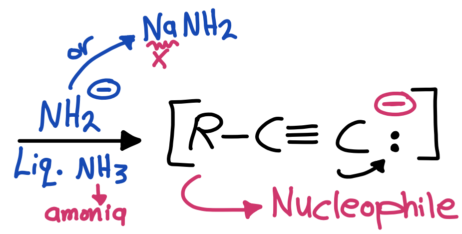
This equilibrium is called : tautomerization.

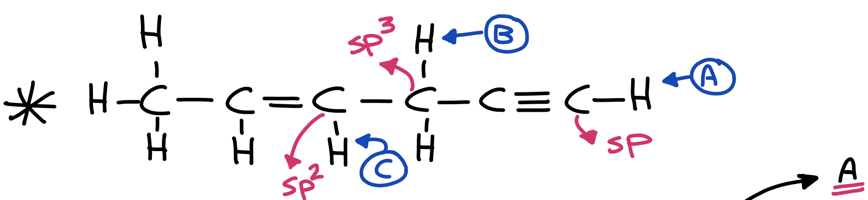


major product

e) With strong base ($NaNH_2$) :

Terminal alkyne (R−C≡C−H)





* Which hydrogen is the most acidic ? → A

It based on the Hybridization of the attatched Carbon. For Sp-Carbon ⇒ hydrogen is the most acidic, while for sp^3 -hybridized carbon ⇒ the acidity is the weakest.

S-character :	sp	sp^2	sp^3
	50%	~33%	25%

* As S-character of Carbon atom increases ⇒ the electronegativity increases.

The end of chapter 3.